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Electrochemical Properties of High Surface Area Vanadium Oxide Aerogels

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This article explores the effects of surface area and pore volume on the electrochemical behavior of high surface area V_2O_5 gels dried by either supercritical or ambient methods. Traditional composite electrode structures have prevented truly quantitative analysis of surface area effects in nanoscale battery materials, as well as a study of their innate electrochemical behavior. These limitations can be overcome by using the 'sticky-carbon' electrode technique, which provides a direct electroanalysis of the active material without the use of a composite electrode structure. The resulting electrochemical measurements show pseudocapacitive behavior (1000 - 2000 F/g) that has not previously been seen for V_2O_5 aerogels. The relationship between capacitance and pore accessibility is investigated.

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Aerogels are composed of a three-dimensional network of nanometer-sized solid particles surrounded by a continuous macroporous and mesoporous volume. The characteristic mesoporosity of these materials provides both molecular accessibility and rapid mass transport via diffusion. As a result, numerous aerogel compositions have been investigated for heterogeneous catalytic materials.^{1,2} These same physical features should also be desirable for electrochemical materials, e.g., the electrolyte can penetrate into the entire aerogel particle through the mesoporous network. Only a few aerogel systems have been reported as electrochemical materials, but good electrochemical properties have been observed. The vanadium oxide aerogels ($V_2O_5 \cdot nH_2O$) exhibit enhanced lithium capacity as compared to V_2O_5 xerogels or 'crystalline' V_2O_5 ,³ and hold considerable promise for battery applications. The specific lithium capacity for V_2O_5 aerogels is quite good (410 mAh/g at C/40 discharge rate) and decreases only $\sim 25\%$ as the discharge rate increases tenfold from C/40 to C/4.⁴ The electrochemical behavior of another system, based on a mixed ruthenium oxide/titanium oxide composition, has shown that aerogels serve as amplifiers of surface-dominated effects, specifically, charge transport is dominated by the hydrous ruthenium oxide surface.⁵ Controlling the level of hydration is critical for developing extremely high specific proton capacitance in hydrous ruthenium oxide systems.^{6,7}

In characterizing the electrochemical properties of aerogels, powdered aerogels are generally mixed with other components (carbon conductor, polymer binder, and solvent) to form a composite electrode structure. The aerogel particles subsequently agglomerate in this process, which reduces their surface area and alters their porous structure. Thus, the observed response may not necessarily represent the electrochemical properties of the actual aerogel, but rather the behavior of an agglomerated aerogel system. The "sticky-carbon" electrode described by Long and Rolison circumvents these limitations.⁸ By mixing acetylene black and wax (approximately 70: 30 weight ratio), it is possible to prepare a conductive electrode with a

sticky surface that effectively holds a quantitative amount of (finely dispersed) high-surface-area particles, exposes these particles to the electrolyte, and provides good electrical contact to each particle. Using the 'sticky carbon' approach, Long et al. were able to measure the theoretical specific capacitance value for hydrous ruthenium oxide (900 F/g).⁷ The value obtained for this material in a standard composite electrode structure is approximately 25% lower.⁶ The present paper adapts the sticky-carbon method to characterize a series of vanadium oxide aerogels with varying surface areas and pore volumes in order to determine how the electrochemical behavior of the native mesoporous material compares to that of a V_2O_5 -carbon-binder electrode structure.

The two different types of aerogels investigated in this study differed by the manner in which the precursor gels, prepared by the sol-gel method, underwent solvent removal. The samples termed 'scd aerogels' used supercritical drying as described previously.⁹ An ambient-pressure approach (termed 'ambigels') was accomplished by drying the precursor gel using nonpolar solvents such as hexane and cyclohexane.¹⁰ By using these two methods, mesoporous vanadium oxide materials with surface areas ranging from $\sim 150 \text{ m}^2/\text{g}$ to $300 \text{ m}^2/\text{g}$ were synthesized (Table 1). For comparison, a low surface area vanadium oxide xerogel ($< 10 \text{ m}^2/\text{g}$) was also investigated.

Electrochemical properties for both types of V_2O_5 aerogels were determined using the sticky-carbon electrode technique.⁸ The sticky carbon is coated onto a stainless steel current collector by spreading with a spatula. Small amounts of aerogel powder are weighed on a micro-balance and then lightly pressed onto the surface of the wax-acetylene black composite. After pressing, the remaining powder on the weighing paper is measured again. The difference, $\sim 0.5 \pm 0.02 \text{ mg}$, represents the mass captured by the sticky carbon electrode. This method ensures that each particulate is individually wired to the electrode and well exposed to the electrolyte. Electrochemical measurements were performed in an Ar-filled glove box using

a conventional three-electrode cell with lithium foil reference and counter electrodes. The working electrode was either the sticky carbon by itself or modified with V_2O_5 aerogel powder. Two different electrolytes were used; 1.0 M lithium perchlorate in anhydrous propylene carbonate (Aldrich) or 0.1 M tetrabutylammonium perchlorate (TBAP, Acros Organics) in propylene carbonate.

The voltammetric responses for the aerogel immobilized on sticky carbon are shown in Fig. 1a and 1b. In 1.0 M $LiClO_4$ /propylene carbonate, the faradaic features are broad and capacitive for the two different scan rates shown here. At the slower scan rate intercalation peaks appear superimposed upon the capacitive response (Fig. 1a). The background from the sticky-carbon electrode is negligible on the current scale of Fig. 1. At the higher scan rate, the aerogel is responding as a capacitor (Fig. 1b). The direct electrochemical response of V_2O_5 aerogel differs substantially from that obtained for a V_2O_5 aerogel-based composite electrode structure, which displays the characteristic intercalation behavior for sol-gel-derived V_2O_5 materials (Fig. 1c).¹¹

Specific capacitance and multipoint BET surface areas and pore volumes are listed in Table 1 for the various samples investigated in this work. The specific Li-ion capacitance values for the V_2O_5 aerogels range from 960 F/g to over 2000 F/g depending upon the drying process utilized. The largest specific capacitance was obtained with an ambigel that used cyclohexane as the drying solvent (2150 F/g, which, based on the BET surface area, corresponds to nearly 1400 $\mu F/cm^2$). It is interesting to note in Table 1 that this material does not exhibit the largest surface area for the aerogels, but does possess the greatest pore volume. The specific capacitance values for all the V_2O_5 mesoporous samples are greater than that reported for proton-electron insertion into hydrous RuO_2 which is regarded as an excellent pseudocapacitor material.^{6,7,12}

The capacitive response in TBA^+ electrolyte for the aerogel immobilized on the sticky carbon is greater than that of the sticky-carbon background, but significantly lower than in Li^+ electrolyte (Fig. 2). The capacitance per unit BET area for this sample is $50 \mu\text{F}/\text{cm}^2$, which is consistent with (although slightly larger than) true surface-area-normalized double-layer capacitance at smooth electrodes.¹³ This experiment represents a control in the sense that with the larger ionic diameter of the TBA^+ ($\sim 9 \text{ \AA}$ ¹⁴) relative to (unsolvated) Li^+ , only double-layer adsorption of the ion is expected rather than ion insertion into the V_2O_5 . The substantially greater voltammetric charge obtained in Li^+ electrolyte ($460 \mu\text{F}/\text{cm}^2$) underscores the importance of ion incorporation into the V_2O_5 structure.

The data in Table 1 suggest that the specific capacitance (farads of charge stored per gram of V_2O_5) does not necessarily correlate with the N_2 -accessible surface area of the V_2O_5 aerogel. In contrast, there is generally a linear relationship between specific capacitance and pore volume for the various samples (Fig. 3). This behavior highlights the issue of lithium-ion and solvent accessibility to the high surface area of the V_2O_5 network. The scd aerogels have high surface areas and moderate pore volume, but many of the pores in the sample have diameters $< 5 \text{ nm}$. (Fig. 4) If these small pores are not accessible to ions and solvent on an electrochemical time scale, they will not contribute to the overall capacitance of the sample; i.e., these interfaces may not be electrifiable. In contrast, samples dried with a low surface tension solvent at ambient pressure experience some pore collapse and shrinkage, leading to a lower surface area, but they have a narrower pore size distribution ($\sim 25 \text{ nm} \pm 10 \text{ nm}$) with no or few pores sized less than 5 nm . On the basis of the magnitude of the capillary pressure during drying (Eq. 1), it is expected that pore collapse occurs most readily in the smallest diameter pores:

$$P_c = (4 \gamma_L \cos \theta) / d \quad (1)$$

where γ_L is the surface tension of the drying solvent; d is the pore diameter; and θ is the contact angle between the solvent and the pore wall. Even with the collapse of pores < 5 nm in size, the V_2O_5 ambigels retain a high pore volume.

Figure 4 shows the difference in pore size distribution between scd aerogels and ambigels. Most of the pores in the ambigels concentrate between 10 and 30 nm, where electrolyte penetration is not likely to be impeded, and relatively little pore volume is associated with pore diameters < 5 nm as compared to the scd aerogels. While pore volume may be a better parameter to associate with the specific capacitance than total surface area, the scatter in the data in Fig. 3 suggest that total pore volume is not ideal, and a parameter based on pore size distribution may be more relevant.

The voltammograms obtained for both types of V_2O_5 aerogels immobilized on the sticky-carbon electrode are entirely different from those that occur using a traditional composite electrode. The sticky-carbon voltammograms are dominated by a capacitive response and the magnitude of the voltammetric charge indicates pseudocapacitive rather than double-layer capacitive behavior. The fact that pseudocapacitance is observed rather than double-layer capacitance is not surprising in view of the similarities between intercalation and pseudocapacitance.¹⁵ The high capacitance of V_2O_5 aerogels agrees with previous results based on low-frequency impedance spectroscopy, which calculated that a limiting capacitance could be reached in excess of 20,000 F/g.¹⁶ However, the voltammogram reported in that study was representative of intercalation processes as seen for composite electrodes (i.e., similar to Fig. 1c).

The innate electrochemical character of scd aerogels and ambigels can be observed using the sticky-carbon approach. Electron, ion and solvent transport to the networked, nanoscale V_2O_5 is enhanced as compared to the traditional composite electrode structure. That is, the sticky-carbon electrode effectively contacts the gel particulates to the current

collector and permits unrestricted electrolyte access to the surface-confined particulates. In contrast, composite electrodes are characterized by aggregation of particles and occlusion within the multi-component structure, which leads to micrometer-scale dimensions for electron and ion transport. The composite microstructure does not preclude the prospect of excellent battery performance, as was reported in the initial studies. Perhaps the interesting caveat here is that directly "wiring" the aerogel to the current collector circumvents semi-infinite diffusion-limited kinetics and leads to the fundamental response of the nanoscale transition metal oxide.

An intriguing question to be resolved with V_2O_5 (and other transition metal oxide) aerogels is the nature of the sites involved in the enhanced lithium-ion specific capacitance. Because high surface area aerogels amplify surface effects, surface defects that are not normally evident in bulk materials now become prominent. In the case of V_2O_5 aerogels, the prospect of having vanadium vacancies at the more highly defective surface could account for part of the observed and large capacitive response; Li^+ access to such sites simply provides charge compensation for the vacancies. Interestingly, such a mechanism would not necessarily involve electron transfer to the vanadium in the structure, only its defects are affected. Aggregation of the aerogel particles, as occurs in a composite electrode, would minimize the influence of defects. The defect chemistry of V_2O_5 aerogels is presently being investigated.

Acknowledgments

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Table 1. Specific capacitances, surface areas and total pore volumes for vanadium oxide scd aerogel, ambigel, and xerogel.^a

Drying Solvent	Specific Capacitance ^b (F/g)	Surface Area ^c (m ² /g)	Total Pore Volume ^c (cm ³ /g)
Cyclohexane	2150	155	0.87
Heptane	1660	200	0.60
Hexane	1240	165	0.40
Pentane	960	180	0.48
Supercritical CO ₂ (aerogel)	1300 140 (TBA ⁺)	280	0.50
Acetone (xerogel)	620 40 (TBA ⁺)	<10	<0.01

^a Li⁺ electrolyte used unless otherwise noted.

^b Capacitances obtained from the respective voltammograms (at 0.1 mV/s) using the relation $C = I / (dV/dt)$. Capacitances were averaged by measuring the current every 10 mV over the range 3.2 to 1.8 V.

^c Surface area and total pore volume were determined using multipoint BET with Micromeritics ASAP 2010.

Figure Captions

Fig. 1. Voltammograms for V_2O_5 scd aerogels. a) Sticky-carbon electrode, at 0.1 mV/s; b) sticky-carbon electrode, at 5 mV/s; and c) composite electrode, consisting of V_2O_5 scd aerogel, carbon, and PVDF, at 0.1 mV/s. The electrolyte is 1.0 M $LiClO_4$ in PC. The dashed line shows the sticky-carbon background. The arrows in a and c refer to the same voltages.

Fig. 2. Voltammograms (at 0.1 mV/s) for the sticky-carbon electrode and for 0.5 mg of scd aerogel pressed on the sticky-carbon electrode. The electrolyte is 0.1 M TBAP in PC. The second cycle scan is shown here. The first cycle has an irreversible peak at 2.6 V.

Fig. 3. Specific capacitance for V_2O_5 scd aerogel, ambigel and xerogel samples as a function of total pore volume.

Fig. 4. Pore size distribution for V_2O_5 scd aerogel and ambigel (dried in pentane) samples. Most of the pore volume in the ambigel occurs between 10 and 30 nm whereas the scd aerogel has a broad pore size distribution.

Fig. 1

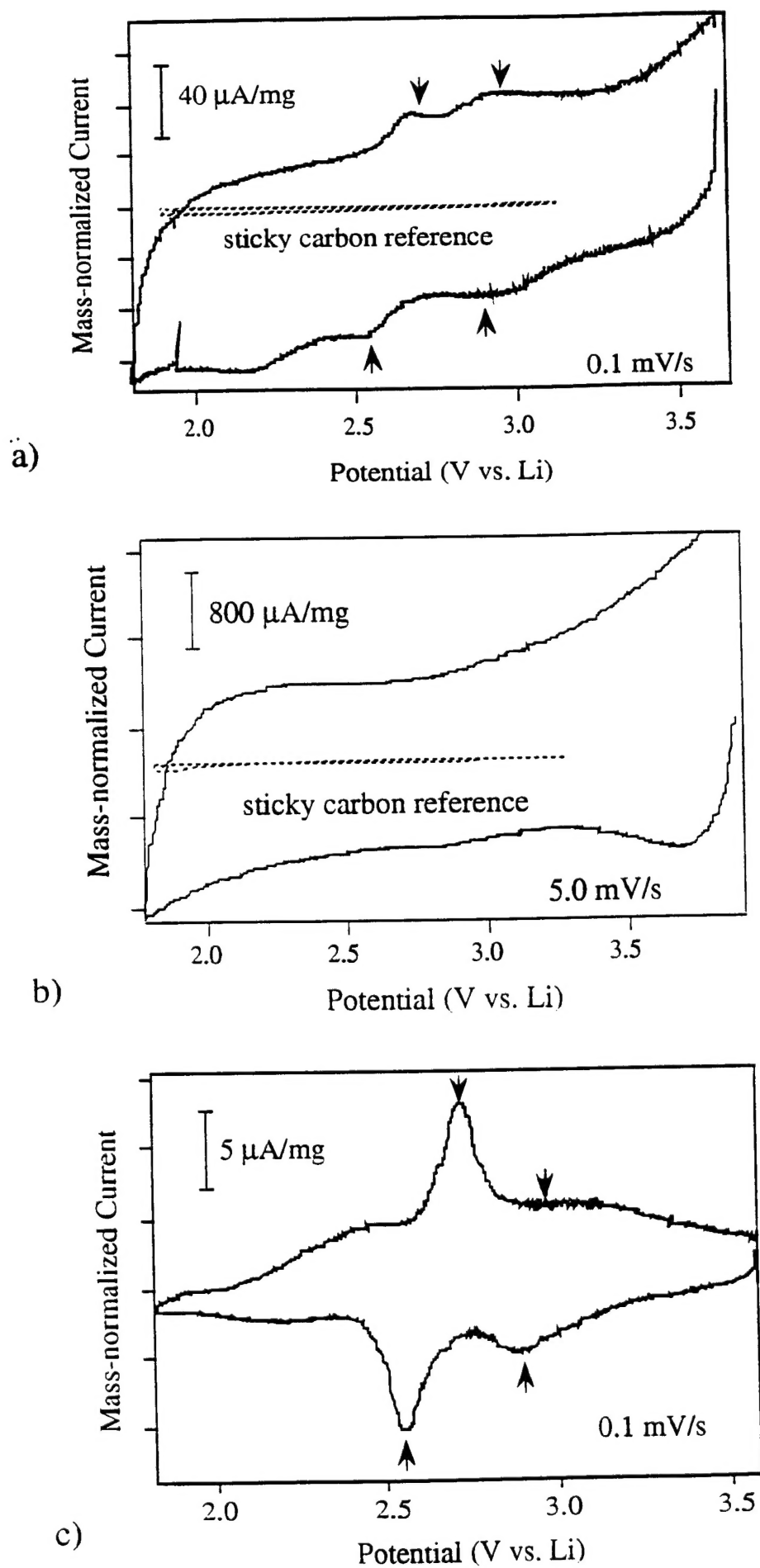


Fig. 2

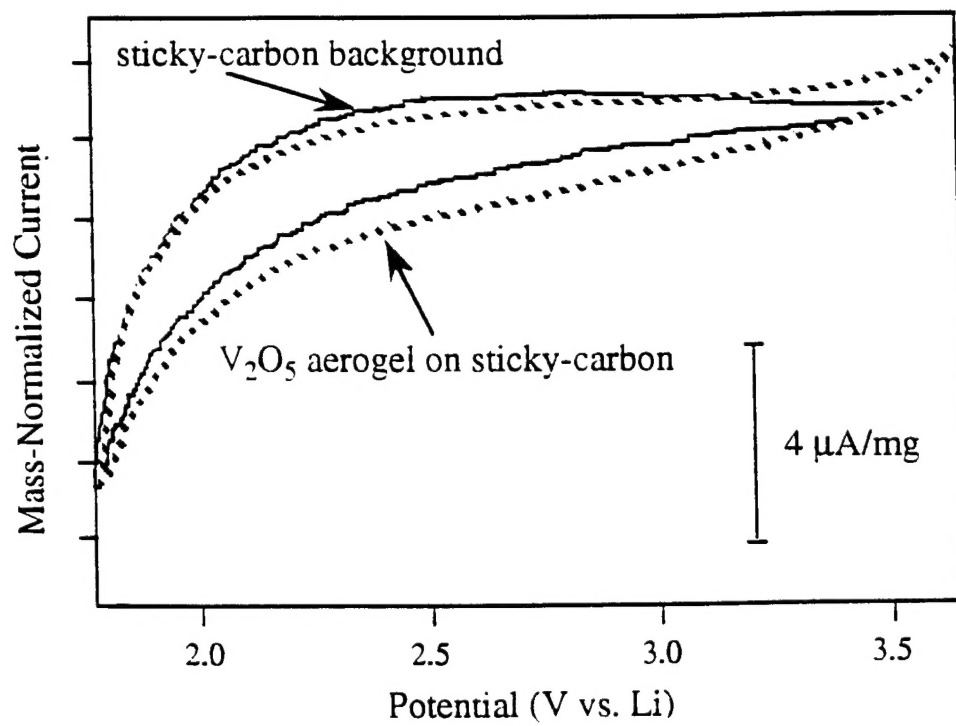


Fig. 3

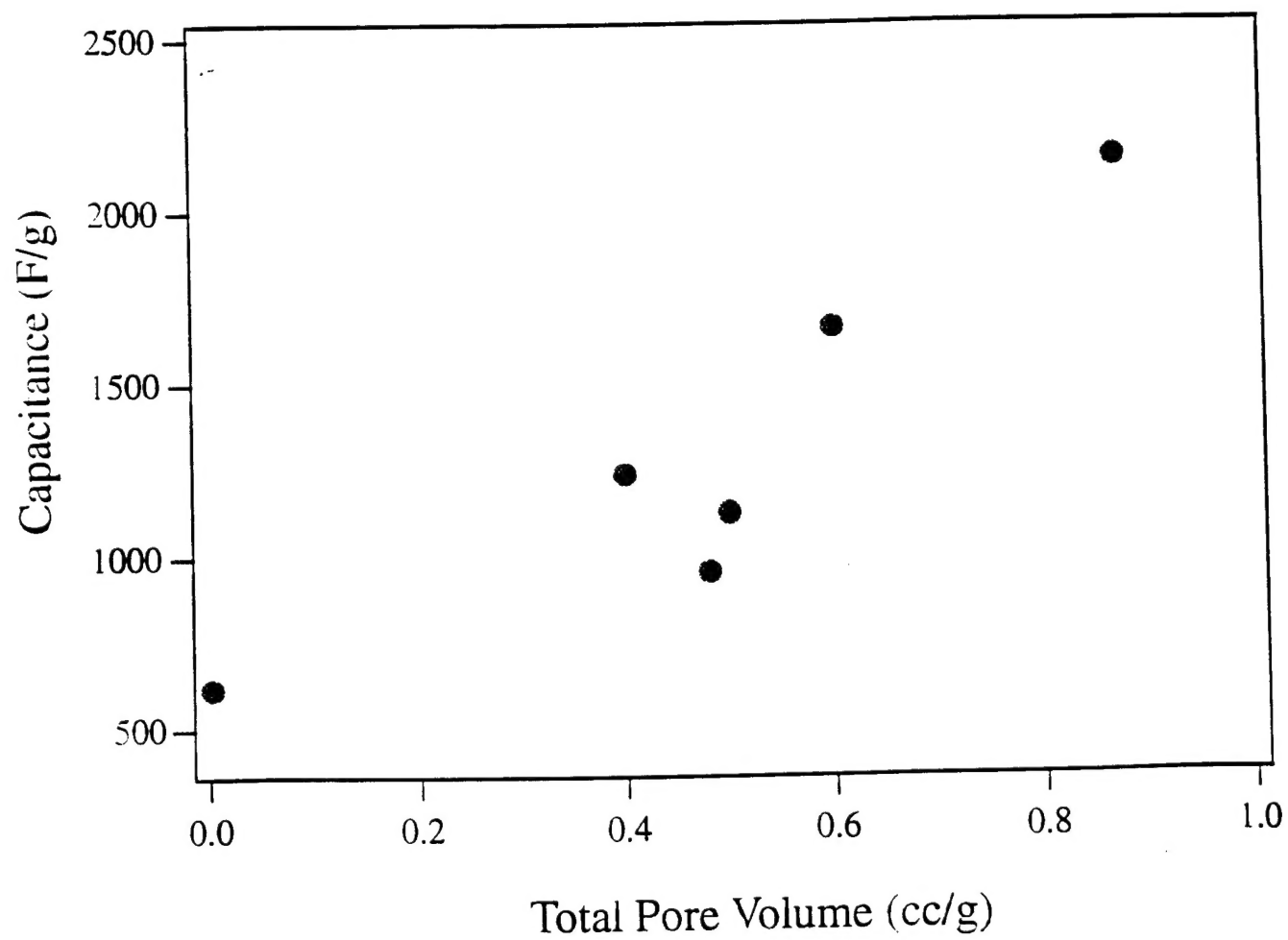


Fig. 4

